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Supplementary Cementitious Materials: New Sources, Characterization, and Performance Insights

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Abstract

Conventional supplementary cementitious materials (SCMs), such as blast furnace slags or fly ashes, have been used for many decades, and a large body of knowledge has been collected regarding their compositional make-up and their impacts on cement hydration and concrete properties. This accumulated empirical experience can provide a solid, confident base to go beyond the status quo and develop a new generation of low-clinker cements composed of new types and combinations of SCMs. The need for new sources of SCMs has never been greater, as supplies of traditional SCMs are becoming restricted, and the demand for SCMs to reduce CO_2 emissions from concrete production is increasing. In this paper, recent research on emerging SCM sources is reviewed, along with new developments in characterizing and qualifying SCMs for use and improved knowledge of SCMs on long-term concrete performance and durability.

Keywords

(B) Characterization; (C) Durability; (D) Blended Cement; (D) Filler; (D) Pozzolan

1.0 Introduction

Supplementary cementitious materials (SCMs) are soluble siliceous, aluminosiliceous, or calcium aluminosiliceous powders used as partial replacements of clinker in cements or as partial replacements of portland cement in concrete mixtures. Many of the materials currently used as SCMs are by-products of other industries, such as fly ash from coal-fired power plants. Some are natural minerals whose energy input in processing is much lower than that used in the manufacturing of portland cement. For example, portland cement clinker has a thermal energy intensity of 3.5 GJ/t clinker [1]. The thermal energy input for fly ash production can be arguably allocated to power production, and not allocated to the fly ash waste product [2]. The calcination of kaolinite clay to make a metakaolin SCM, for example, has a thermal energy input of 0.35 GJ/t clay [1], only 10% of that of portland cement clinker. The energy used in the production of uncalcined natural pozzolans, such as pumicites, is necessarily much lower. Accordingly, life cycle analyses demonstrate a significant reduction in energy use and greenhouse gas emissions associated with concrete mixtures when SCMs are used [3–5].

SCMs currently serve as one of the primary tools for reducing carbon dioxide emissions associated with concrete production. While in 2009 the Cement Technology Roadmap [6] identified four levers for reducing emissions, including thermal and electric efficiency, alternative fuels, clinker substitution, and carbon capture and storage, it is becoming apparent that the use of SCMs as partial clinker substitutes is the strategy with the lowest economic and performance impacts to cement and concrete production. Indeed, a recent investigation commissioned by the United Nations Environmental Program Sustainable Building and Climate Initiative (UNEP-SBCI) [7] identified clinker substitution and concrete mixture proportioning as the most favorable carbon reduction levers for the industry. Other strategies may become more feasible in a carbon-taxed economy [8].

The concrete industry also relies on SCMs to improve the long-term mechanical performance and long-term durability of concrete mixtures, both of which play a role in improving efficiency of concrete mixture designs (e.g. increasing strength-to-mass ratios) and increasing longevity, thereby impacting associated emissions over a concrete structure's lifetime [5,7]. The use of SCMs in modern concrete mixtures, therefore, is nearly ubiquitous. Herein lies a problem. The industry has traditionally been dependent on industrial waste streams as the main source for SCMs, e.g. fly ash, ground granulated blast furnace slag, and silica fume. However, in the case of fly ash in particular, the supply chain is threatened. In the US, approximately 40% of coal-fired power plants have closed in the last five years; the UK plans to retire all of its coal-fired power plants by 2025 [9] and the Netherlands by 2030. Furthermore, the demand for cement continues to increase, with demand projected to increase to over 6 Gt by 2050 [7]. The industry is changing rapidly, with increases in imports/exports of SCMs between countries [10] and development of new resources for SCMs, the latter of which will be discussed further in this paper.

Hand in hand with the exploration of new sources of SCMs comes the demand to test and qualify these materials for use. It is becoming increasingly apparent that our traditional, standardized test methods to determine reactivity, among other properties, were developed for sources we already know (e.g. fly ash) and are not appropriate for screening alternative sources of materials with different properties [11,12]. Hence, researchers are developing new test methods to characterize novel SCMs, addressed in this paper.

Research on supplementary cementitious materials is becoming increasingly important. We are moving beyond the testing of small-scale sources for incremental effects on properties and are starting to devise a new system to comprehensively and holistically evaluate any new material to enable its use in concrete materials, thereby expanding our available material resources rather than contracting them. In this paper we explore the new (and re-newed) materials being considered for use as SCMs, new strategies for materials testing and characterization, and new knowledge on the impacts of SCMs on critical aspects of concrete long-term durability.

2. New Sources of SCMs

A wide variety of materials are available for use as SCMs, including raw and calcined natural minerals, biomass ashes, and industrial by products. Some of these materials are described in Table 1, intended to showcase the variety and availability of SCM resources.

2.1 Natural SCMs

To find new SCMs for modern concrete production one can start by looking to the past, at concrete's origins in the Roman cements made from volcanic tuffs. Volcanic materials, including tuffs, ashes, pumicites, perlites and zeolites, can be excellent natural pozzolans, with high amorphous silica and alumina contents, as reviewed recently in a RILEM State-of-the-Art Report [13]. With the increased need for SCMs and shortages in many commonly used materials, natural SCMs are experiencing a sort of renaissance. In the US, a new trade group started in 2017, the Natural Pozzolan Association (NPA), to represent the interests of this growing industry. Natural pozzolans played a strong role in the history of concrete, from ancient times and in the early 20th century [14]. However, they do not have widespread availability and, until recently, they have not been cost-competitive with fly ash and slag. The landscape for natural SCMs is changing, though, and the NPA reports that production capacity is increasing on the order of 500 Kt per year in the US in 2018 and 2019 [15]; this resurgence is accompanied by new research.

Table 1. Overview of materials used or considered as SCMs [16]. Permission to reprint is provided by a Creative Commons Attribution 4.0 International License.

Material	Chemistry	Used as SCM (Mt/y)	Total volume est. (Mt/y)	Comments
Blast furnace slag	Ca-Si-Al	330	300-360	Nearly fully used, latent hydraulic
Coal fly ash	Si-Al	330-400	700-1100	Subject to limitations on carbon content, reactivity
Natural pozzolans	Si-Al	75	Large accessible reserves	Large variety/variability, often high water demand
Silica fume	Si	0.5-1	1-2.5	Used in high-performance concrete
Calcined clays	Si-Al	3	Large accessible reserves	Metakaolin performs best, often high water demand
Limestone	$CaCO_3$	300	Large accessible reserves	Cementitious contribution in combination with reactive aluminates
Biomass ash	Si	0	100-140	Competition with use as soil amendment, high water demand, (for some: high alkali contents)
MSWI bottom ash	Si-Al-Ca	0	30-60	Expansive and corrosive components, leaching issues
Steel slag	Ca-Si-Fe	0 (negligible)	170-250	Various types, can contain expansive components (CaO) or leachable heavy metals (Cr,…). Low reactivity
Copper slag	Fe-Si	0 (some as filler)	30-40	Low reactivity, leaching of heavy metals, more research needed
Other non-ferro slags	Fe-(Si)-(Ca)	0 (some as filler)	5-15 Mt/y each (FeCr, Pb, Ni)	Low reactivity, leaching of heavy metals, more research needed

Bauxite residue	Fe-Al-Si	0	100-150	High alkali content, low reactivity, colour
Waste glass	Si-Na-Ca	0 (or negligible)	50-100	Glass recycling preferable, high alkali content

In a paper showcasing new sources of SCMs, Diaz-Loya et al. [17] included natural SCMs, a pumice, perlite, and vitric ash, that all performed similarly to a Class F fly ash, but are in fact more pozzolanic (as indicated by calcium hydroxide consumption in cement pastes). Ghafari et al. [18] also examined perlite and pumice. In spite of frequent concerns that natural SCMs reduce workability, the perlite was not detrimental to fresh state properties. The pumice provided the best strength enhancement, but increased water reducer demand [18]. The impact of pumice and perlite on water demand is related to the particle size distribution; the pozzolanicity of both increases with increased fineness (as measured by calcium hydroxide consumption) [19], but water demand or plastic viscosity also increase (Figure 1) [20–22]. This suggests that the impact of pumice and perlite on reactivity and water demand can be balanced by selection of particle size distribution during grinding or through the use of chemical admixtures. Intergrinding of SCMs with clinker or cement is also possible, and can help when trying to achieve an optimal particle size distribution of the components in blended cement systems [23].

The impact of natural SCMs on water demand is not only controlled by fineness, but also by specific surface area. Natural zeolites are very porous and have a high internal surface area, thus they have a strong impact on workability [18,24]. It has been shown that calcination of natural zeolites reduces internal surface area, which in turn reduces the viscosity and yield stress of zeolite-cement paste mixtures [24]. Calcination also serves to dehydroxylate smectite clay impurities present in zeolites, also contributing to reduced water demand [24]. Chemical and mechanical treatments have also been shown to modify zeolite reactivity. Burris and Juenger [25] showed that treating natural zeolites with acids de-aluminates them, increasing surface area and thus pozzolanic reactivity (as measured by calcium hydroxide consumption). Likewise, milling zeolites decreases particle size, increasing filler effects and pozzolanic reactivity [26]. The high internal surface area of zeolites also provides unique opportunities for improved concrete performance, such as enhanced internal curing to reduce autogenous shrinkage [27] or self-healing of cracks [28].

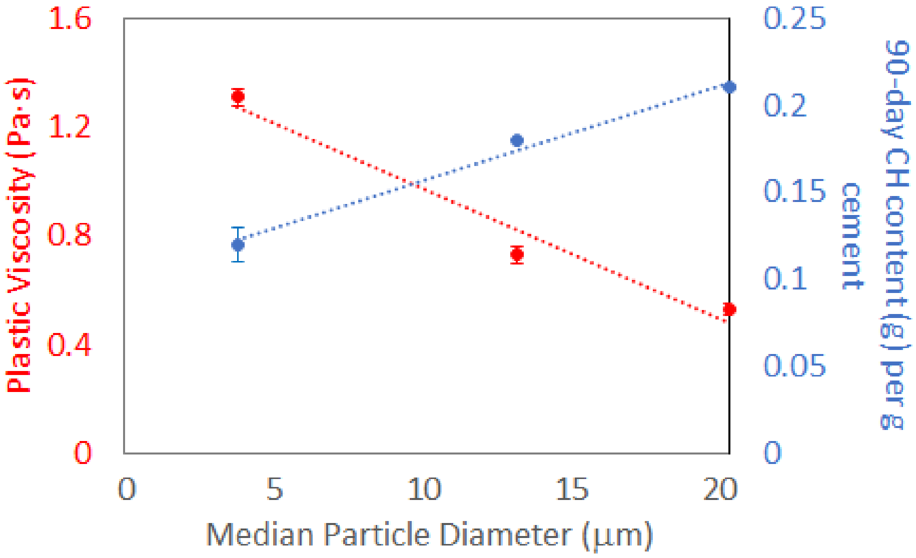

Figure 1. Impact of pumice particle size on the calcium hydroxide (CH) content and plastic viscosity of cement pastes containing 20 wt.% pumice. Higher CH contents suggest less pozzolanic reaction. Higher plastic viscosity indicates higher water demand. Data from [20].

At the moment, in many regions the cost of quarrying, processing, and transporting natural SCMs may be cost-prohibitive compared to waste-derived SCMs (though this may change as supply/demand shifts). Therefore, there is some interest in exploring natural SCMs derived from waste streams. For example, relatively pure pumicite quarried for other industries may have a layer of overburden, or less pure pumicite. Such overburden pumicite does not have a pure white color and has a lower amorphous content, but is still pozzolanically reactive and suitable as an SCM [12,29]. New material sources should be approached with caution, however, as some mineral waste streams are not suitable as SCMs. For example, quartz and other mineral fines have been shown to pass ASTM C618 [30] specifications for natural pozzolans, even though they are not pozzolanic [12]. This example, along with countless examples from the literature of cement replacements with inert materials, demonstrate the need for better testing, as discussed in Section 3 of this paper.

2.2 Calcined Natural SCMs

Calcined sedimentary materials are also an excellent source of natural SCMs. Calcined kaolinite clay, or metakaolin, has a strong history of use as an SCM in concrete [31]. However, the relatively pure metakaolin that is commonly used as an SCM is also costly because it has limited availability and has value for other industries. Thus, there is interest in calcining other clay minerals and impure clays for use as SCMs. While some clay minerals, such as illite and hectorite, can be dehydroxylated by calcination, they remain inert in cementitious mixtures [32]. Calcined smectite, bentonite, or montmorillonite clays, on the other hand, can be pozzolanically reactive [31–34]. In a study of several purified clay minerals, Hollanders et al. [32] found that calcium-rich smectites are slightly more reactive than sodium-rich ones because they become more amorphous on calcination. Also, smectite clays agglomerate during calcination, reducing specific surface area. With respect to kaolinite, Hollanders et al. [32] found that the degree of ordering of the original kaolinite affects its reactivity after calcination, with higher ordering needing a higher calcination temperature to achieve equivalent amorphization and thus pozzolanicity (as measured by calcium hydroxide consumption). Danner et al. [34] found that calcined kaolinite released more silicon and aluminum into solution than calcined montmorillonite, probably accounting for the increased reactivity of metakaolin (Figure 2).

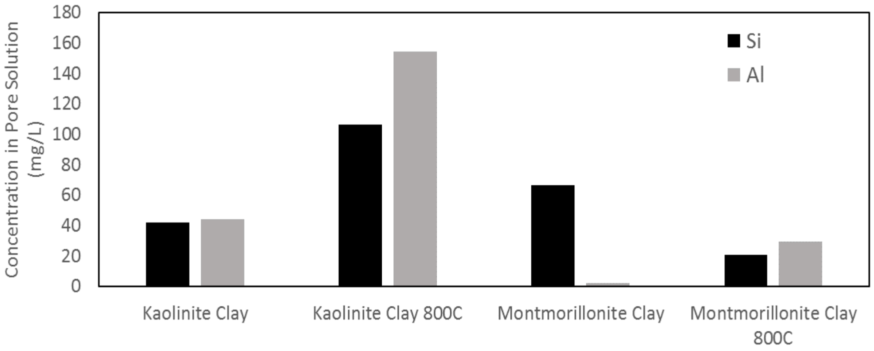

Figure 2. Concentrations of silicon and aluminum released into a simulated concrete pore solution by clays containing 47 wt.% kaolinite or 54 wt.% montmorillonite in their original and calcined states. Data from [34].

Knowledge of the pozzolanicity of smectite clays can be employed to take advantage of low-kaolinite clays as SCM sources. For example, Taylor-Lange et al. [33] tested a clay made by blending kaolinite and sodium-bentonite and also a natural impure clay that contained a high quantity of inert minerals in addition to kaolinite and montmorillonite. They found both to be moderately pozzolanically reactive, as measured by calcium hydroxide consumption. Alujas et al. [35] tested a 40 wt.% kaolinite, 40 wt.% smectite clay and determined that the role of this calcined clay in cementitious systems was part pozzolanic, which increased later age strength, and part filler effect, enhancing early age strength through increased cement hydration. Schulze and Rickert [36] examined 15 different clays of varying purity and compositions. They found that there was no correlation between compressive strength and reactive silica content of the clay, so other characterization methods are necessary to predict reactivity. Clearly, interest in impure clays as SCMs is increasing, and industrial trials have begun to take these from the laboratory into practice [37].

As with volcanic minerals, it is of interest to reduce cost of calcined clay SCMs by looking to wastes and byproducts of other industries and to underused materials. Snellings et al. [38,39] have looked at clay-rich dredged sediments, for example. Ports, harbors, and waterways are routinely dredged, and the sediments are mechanically de-watered and stockpiled. These sediments may contain clays, so can be calcined and used as SCMs. The calcined sediments from the Port of Antwerp studied by Snellings et al. [39] were more pozzolanic than a fly ash, as measured through heat released from pozzolanic reactions, and the calcined material was found to be free of organic content and have a high amorphous content. Zhou et al. [40], similarly, examined calcined excavated waste clay from London, which contained clay minerals and was shown to be pozzolanic, as measured by the Frattini test. Suraneni et al. [41] and Seraj et al. [42] have found waste fines from the production of lightweight fine aggregates made from calcination of slates and shales to be pozzolanic and suitable as SCMs.

2.3 LC^3 Materials

The worldwide availability of impure clays, their good performance as SCMs, and the observed interaction of aluminosiliceous SCMs with limestone additions to form additional reaction products has resulted in the extensive development of a binder system called LC^3 (limestone-calcined clay cement). A recent paper by Scrivener et al. [43] provides an extensive review of this system. The proportions of components can vary, but the most promising combination is one called LC^3-50, which contains 50% clinker, 30% calcined clay, 15% limestone, and 5% gypsum. Concrete made with LC^3 can achieve improved mechanical properties and permeability compared to concrete with similar mixture proportions containing OPC and 30% fly ash [44]. The calcined clay can be impure, but should have at least 40% kaolinite, since clays with lower amounts of kaolinite are not as pozzolanically reactive (Figure

3a). Interestingly, clays with higher kaolinite contents actually cause the hydration of the clinker phases to slow down by 28 days due to pore refinement [45], Figure 3b. Similarly, metakaolin can slow cement hydration by increasing the release of aluminum into solution, inhibiting nucleation of calcium silicate hydrate (C-S-H) [46] or slowing down alite hydration. However, since the reaction of the metakaolin continues in these situations, reacting with limestone to form carboaluminates, strength gain continues. The same effects can be seen when dolomitic limestone is used, since these materials contain reactive calcite [47], and dolomite has been shown to be unreactive at room temperature [48]. Also worth considering is the composition of the cement blended with the limestone and calcined clay. Fernandez et al. [49] showed that in ternary cement-SCM-limestone systems, the C_3A content and alkali content of the cement impact the reaction of the limestone. Carboaluminates and hydrotalcite are only formed at the expense of monosulfoaluminate at early ages when C_3A and alkalis are high, while they form at later ages regardless. This effect influences the rate of reaction and strength gain in these systems.

Increasing knowledge about LC^3 is helping it move from the laboratory to the field. There have been successful industrial trials of LC^3 in Cuba [50] and India [51], with interest in changing standards to allow classification and implementation of this materials [43].

Coupled with increasing interest into LC^3 is an increase in research into the role limestone plays in cementitious systems. For example, Bentz et al. [52] found that high volumes of limestone addition have little impact on setting because the particles play an active role in the development of the percolated structure that determines setting. It has also been shown that limestone is a better filler than quartz, not only because of the formation of carboaluminate phases, but because C-S-H sorbs CO_3^{2-} ions that the limestone releases into solution, then the C-S-H releases OH- into the pore solution through ion exchange, driving C-S-H growth [53]. Additionally, Schöler et al. [54] demonstrated that limestone increases cement hydration kinetics (quantified as an increase in heat flow at the onset of the acceleratory period) because it increases the undersaturation with respect to alite. The effects on rheology are very different between limestone and quartz-based fillers, for a similar volumetric replacement, with a much lower yield stress in limestone-containing mixtures, likely due to increased inter-particle electrostatic repulsion [52]. This result has implications in additive manufacturing applications [55]. Similar to systems containing only a single SCM, like pumice, the particle size in a ternary blended system should be optimized to control and enhance the performance of the components [56].

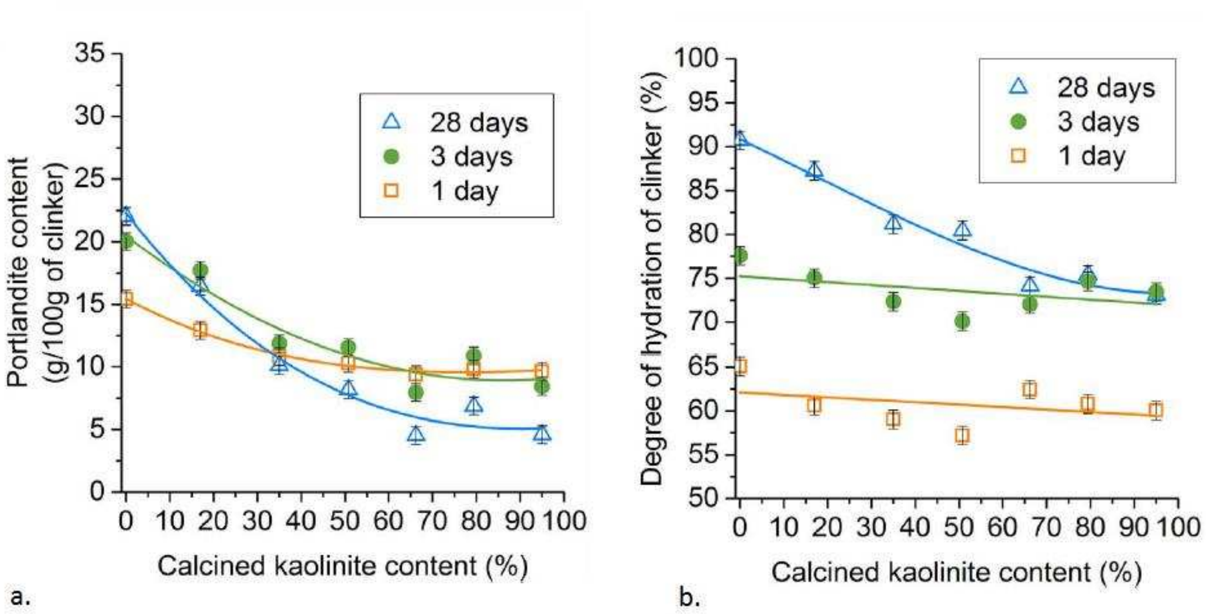

Figure 3. Influence of calcined kaolinite content of impure clays on (a) the portlandite content of cement pastes determined by thermogravimetric analysis and (b) degree of hydration of clinker determined by Rietveld quantitative x-ray diffraction. Reprinted from [45] with permission from Elsevier.

2.4 By-product Materials: Ashes and Glass

Fly ash has been the most commonly used SCM in recent decades, and there continue to be research efforts directed toward understanding its performance, particularly into systems where high volumes of fly ash are combined with fillers and additives to modify performance. Fly ash, like most SCMs, influences strength and setting in complex ways; it behaves like a filler and a pozzolan simultaneously, diluting cement content, and chemically interfering with cement hydration reactions [57]. All of these factors can mask the understanding of fly ash's hydraulic and pozzolanic contributions to strength gain and performance, and it is important to be able to de-couple these effects through research and improved test methods, as discussed in Section 3. Another avenue of research that is relevant for fly ashes and slag is the investigation of the reactivity of glasses present in these materials. Fly ashes contain a variety of glassy phases, mostly modified aluminosilicates [58]. Both calcium and aluminum are important network modifiers in glasses that affect reactivity [59]. Similar to work examining the role of disorder in clay structures on reactivity, the structural rigidity of glasses in fly ashes has also been shown to affect the rate of dissolution [59,60]. Glass dissolution is complex and dependent on the composition of the surrounding solution, and it has been shown that dissolution is hindered in the presence of calcium and aluminum through the formation of precipitated products on the glass surface [61,62].

Paris et al. [63] recently reviewed the literature on waste materials that can be used as SCMs. Beyond fly ash and slag, these include a wide variety of sources, such as agricultural waste ashes [64], ashes from biomass used for fuel [65], municipal waste sludge ash [66], oil shale waste [67], and waste glass [68]. Most waste ashes need pre- or post-treatment to remove organic matter or metals, but can be suitable for use as SCMs. For example, grinding and classification can reduce surface area and remove quartz from sugar cane bagasse ash, thereby increasing reactivity [69–71]. There are three classes of waste glass: container/bottle, plate/window, and E-glass (fiberglass waste), with E-glass having lower production and a lower alkali content than the others. All are pozzolanic and are suitable as SCMs when ground to sufficient fineness and alkali contents are taken into account in mixture design [68].

With shortages in fly ash production in many countries and regions, there is interest in examining the performance of fly ashes and other coal combustion residuals that do not meet current specifications and fly ashes that have been landfilled or ponded. Fly ashes that do not meet specifications can be beneficiated or remediated by blending with other materials, classification or separation, chemical passivation, or thermal beneficiation [72]. For example, Al-Shmaisani et al. [29,73] examined fly ashes beneficiated through chemical treatment for high unburned carbon or blending to meet the chemical and physical requirements for a Class F fly ash. All materials performed well in testing for fresh and mechanical properties and concrete durability compared to a production Class F fly ash. In some cases, it may be possible to use an off-spec fly ash as is, accounting for its impact on performance during concrete mixture design. For example, Zunino et al. [74] looked at high-SO_3 fly ashes, those with SO_3 contents higher than the ASTM C618 [30] limit of 5.0%. These fly ashes result when systems are installed to control flue gas emissions and can cause delays in setting. Zunino et al. [74] found that the delayed setting can be controlled through washing, limestone addition, or through the use of accelerating admixtures.

There are increasing research efforts aimed at reclaiming fly ash from landfills and ponds for use as SCMs. In a recent chapter outlining the issues and opportunities for reclaimed fly ash use, McCarthy et al. [9] reported that there could be up to 50 Mt of stockpiled fly ash in the UK and possibly 1 Gt in the US. China could have 2.5 Gt in reserve [75]. Standard specifications for fly ash do not typically prohibit the use of reclaimed material, as long as it meets the necessary chemical and physical characteristics. Depending on the fly ash and the storage conditions, the fly ash needs to be processed, at least minimally, before use since, over time, the ashes agglomerate and acquire moisture. For example, Diaz-Loya et al. [17] have shown that fly ash placed in landfills in the 1970s and 1980s can have similar characteristics to fly ash produced in 2016 after drying and classifying, and mortars blended with them developed comparable compressive strengths compared to fly ashes stored in silos. Low calcium content ashes did not hydrate, and the phase distributions were essentially unchanged after time in the landfill.

Wirth et al. [76] examined changes in fly ash with weathering and found the presence of hydrated phases in some cases, including calcium sulfates, carbonates and clays, suggesting that compositional changes may occur and should be examined. They also found changes in particle morphology with weathering. Fedorka et al. [77,78] have shown that heating reclaimed fly ash in a proprietary turbulent air system removed organic contaminants, significantly reducing loss on ignition values, making the fly ash suitable for use. Al-Shmaisani et al. [29,73] similarly showed that reclaimed fly ashes perform similarly to production fly ashes, even when moisture contents are slightly higher than allowed by ASTM C618, with differences in performance linked to particle size and shape following grinding or classification.

2.5 By-product Materials: Slags

Ground granulated blastfurnace slag (GGBFS) from pig iron production is one of the most commonly used and valuable SCMs. As a latent hydraulic material GGBFS can substitute for clinker to a large extent (up to 95%) and is well-known for enhancing concrete durability. As a consequence, where economics and logistics allow, GGBFS is practically fully used by cement and concrete producers as an SCM. In contrast to GGBFS, other metallurgical slags have found little application as SCMs for a variety of material-related reasons including low reactivity, the presence of incompatible phases such as free CaO or MgO, and environmental and occupational risks related to the heavy metals contained in some slags. Despite these technical challenges, recent years have seen increasing research in the use of other ferrous and non-ferrous metallurgical slags as SCMs. In particular, carbon steel slags generated in Basic Oxygen Furnace (BOF) or Electric Arc Furnace (EAF) steelmaking have received considerable interest.

Compared to other slags, BOF carbon steel slags contain significantly lower amounts of heavy metals; however, they usually contain free lime or magnesia and non-hydraulic calcium silicate phases. Maturation, a combination of hydration and natural carbonation in open air, is a common practice to reduce the free lime content and avoid volumetric expansion. When added to cementitious mixtures, carbon steel slags have been noted to delay the early hydration of cement and reduce early age strength development [79]. Recent research has shown that this retardation can be mitigated in several ways. For example, Hou et al. [80] showed that precarbonation of the steel slag improved early cement hydration, mitigated volume stability issues, and resulted in a large increase in strength. Elevated temperature curing [79] or carbonation curing [81,82] have also been shown to activate steel slag, resulting in enhanced material performance. Other studies have described activation of carbon steel slag by extensive milling or particle size classification. Shi et al. [83] and Qiang et al. [84] reported clear (latent) hydraulic activity intermediate between fly ash and GGBFS for carbon steel slags of particle sizes below 20 µm. Another approach is to modify the steel slag properties by rapid cooling of the slag or using by oxidizing conditions to enhance the stabilization of the alpha and beta polymorphs of C_2S by Fe^{3+} [85].

Ferrous slags derived from production of stainless steel, alloyed steel, or ferroalloys have somewhat different compositions than carbon steel slags in that they are enriched in Ca-Mg-silicate phases and contain less free lime or magnesia. Heavy metal concentrations and stability are usually more challenging, but depend strongly on the metallurgical process. High-temperature modification of the Ca/Si ratio of stainless steel slag composition can result in beneficial formation of hydraulic phases such as C_3S and alpha or beta C_2S, as shown by Kriskova et al. [86]. Other researchers have looked into using ferronickel and ferrochromium slags. As in case of carbon steel slags, rapid cooling and fine grinding positively influenced the mainly pozzolanic reactivity [87,88] and provide interesting opportunities for application if the environmental quality can be ensured.

Non-ferrous slags are derived from the production of copper, lead, or other metals in pyrometallurgical processes. Most non-ferrous slags are rich in iron, usually present as oxides or silicates. Recent research by Edwin et al. [89,90] has shown that copper slags have only limited pozzolanic reactivity and mostly acted as fillers in concrete. Fine grinding of the slag [89,91] or introduction of calcium in the high temperature slag processing stage [92] have been shown to increase the reactivity of the slag and provide inroads to enabling the use as an SCM. The presence of significant concentrations of heavy metals, such as residual Zn or Pb, in some slags has been noted to delay the early hydration of cement and poses challenges in terms of meeting environmental quality requirements.

3. Advances in SCM Characterization and Testing

To tackle the challenge of a diversifying range of SCMs and to overcome shortcomings in existing standardized test methods, there is a clear need for new SCM characterization and testing methods to achieve a better generic understanding of SCM behavior and to more universally and more reliably predict concrete performance and durability [11]. Over the past few years, this need has been addressed on two distinct levels: 1) advancement of in-depth characterization techniques to determine fundamental SCM properties that, for example, can be used as input for microstructural modelling to predict performance and durability, and 2) development of more reliable, relevant and rapid screening tests that aim to judge SCMs on performance, not on origin, and that can be widely used in research, development and manufacturing control of SCMs.

3.1 Advances in SCM Characterization Techniques

To build physics-based microstructural models of blended cements, the fundamental material properties of SCMs need to be known in considerable detail. This includes data on the chemical and phase composition and on physical properties such as particle size distribution, density and specific surface area. This information can be obtained from established and widely available methods such as X-ray fluorescence (XRF) spectrometry, quantitative X-ray powder diffraction (XRD), thermogravimetry, laser diffractometry, He pycnometry and BET N_2 adsorption, respectively [93]. Even though these analytical techniques may be routinely used and operate on well-known principles, it is crucial to use adapted, well-calibrated measurement procedures and careful interpretation to obtain accurate and precise results. This was clearly demonstrated by recent work of RILEM TC 238-SCM that investigated the applicability of measurement protocols for a wide range of SCMs and formulated recommendations for routine analysis of particle size, surface area and shape [94], or measurement of loss on ignition by thermal analysis [95]. It is clear that adjustments in analytical procedures are required depending on the SCM type and properties, even for seemingly robust techniques. Table 2 summarizes for common SCM characterization techniques what information can be obtained and what are typical assets and limitations for these techniques.

Solid state NMR spectroscopy has contributed much to our understanding of cement hydration by delivering quantitative structural information on cement hydrates. Recent contributions using ^{27}Al and ^{29}Si magic-angle spinning (MAS) NMR added to this by shedding light on relationships between composition, local atomic structure and reactivity of SCMs. Thomsen et al. [96] showed the contrasting impact of alkali versus calcium network modifiers on aluminosilicate glass structure where alkali cations preferentially charge balance AlO_4^{3-} tetrahedra, while calcium ions are more associated to depolymerized SiO_4^{4-} tetrahedra. The resulting local structural heterogeneities in the aluminosilicate glass structure were shown to positively affect reactivity [97]. Similarly, Kinnunen et al. [98] found un-mixing or phase separation of aluminosilicate glasses by rapid cooling to increase glass reactivity in alkaline solutions. Also, for calcined clays, detailed NMR studies contributed to explaining reactivity differences between calcined clays based on differences in local structural ordering and bonding environment of the thermally activated materials [34,99]. In an original approach, Ruiz-Santaquiteria and Skibsted [100] used NMR to characterize the residues of dilute dissolution experiments and identify reactive sites in calcined clays. In the future, advanced solid-state NMR methods such as multiple-quantum magic-angle spinning (MQMAS) could be instrumental in SCM characterization by offering increased spectral resolution for quadrupolar nuclei such as ^{27}Al or ^{23}Na [101]. This was demonstrated recently by the identification of different structural sites of Al in ettringite or ye'elimite [102,103].

Unfortunately NMR spectroscopy cannot be used to study materials containing significant concentrations of paramagnetic ions such as iron. Instead Pair Distribution Function (PDF) analysis of neutron and X-ray scattering data can be used to acquire information on interatomic distances and infer changes in local structure as a function of compositional changes or hydration [104]. Natali et al. [105], for instance, studied different types of Class F fly ash using PDF, showing major changes in fly ash glass atomic structure for high concentrations of aluminum, iron or carbon (graphite).

Table 2. Common SCM characterization techniques summarizing the information probed, assets, and limitations.

Technique	Information	Assets	Limitations
Laser diffractometry	Particle size distribution – size range 0.1 to 1000 µm	Common, rapid, reproducible measurement	Optical model and sample preparation sensitive (disagglomeration, dispersion,…)
He pycnometry	Density	Common, rapid, reproducible, straightforward	Dry sample required, in case of closed porosity not accessible to He an apparent density is measured
BET N_2 sorption	Specific surface area, size and shape of pores	Common, includes internal porosity	Degassing/drying procedure may lead to changes in sample properties, not for coarse materials
Blaine air permeability	Fineness	Reference method for cement, standardised	Not easily amenable to very fine or rough powders
X-Ray Fluorescence spectrometry (XRF)	Chemical composition	Rapid, straightforward, accurate	Calibration with similar reference materials is required to account for matrix effects Preparation of sample beads leads to loss of volatile elements, e.g. alkalis
Thermogravimetric analysis (TGA)	Loss On Ignition, volatiles/thermally unstable phases	Accessible, straightforward, quantitative	Interference between weight changing events (e.g. oxidation, decarbonation,…), dependence on sample size and instrument geometry
X-Ray powder Diffraction (XRD)	Mineralogy, phase composition	Accessible, rapid, multiple phase identification and quantification	Quantitative analysis requires extensive knowledge Amorphous phases give diffuse signal, complex analysis
Solid state Nuclear Magnetic Resonance (NMR)	Local structural order, element specific (^{27}Al, ^{29}Si,…)	Atomic structure information, applicable to	Accessibility of instruments, expert support required

spectroscopy		amorphous phases	
Scanning Electron Microscopy (SEM)	Spatially resolved phase information (size, shape, texture, distribution)	Can be combined with microchemical analysis	Accessibility, sample preparation of polished sections and data interpretation requires expertise, time and resources

One of the most important properties of an SCM is its chemical reactivity in a hydrating portland cement environment. However, it is not straightforward to measure this. In cement pastes, the reaction of the SCM interferes with the hydration of clinker minerals and can be affected by the formulation of the cement [106,107]. To isolate the reaction of the SCM, a common approach is to use simplified model systems. The most elementary approach is to use highly dilute systems in which the rate of dissolution of the SCM can be measured, avoiding precipitation of reaction products [108]. The rate of dissolution can be calculated from the solution composition, using Si or Al dissolved from the SCM in solution as a tracer. These studies demonstrated the close correlation between the atomic structure of the SCM and its reactivity [99]. In particular, the connectivity of the aluminosilicate glass structure was found to correlate with dissolution rates and reactivity in blended cements [59,108,109]. For calcined kaolinite, the dissolution rate using Al as tracer was found to correlate well with reactivity in cement pastes [110]. In addition, dissolution studies have shed new light on the interaction between solution chemistry and SCM reactivity, such as the accelerating effect of pH or the inhibiting effect of dissolved Ca or Al [61,111,112].

For heterogeneous materials, it is of interest to determine physico-chemical properties down to the level of individual components of the SCM. This can be done using electron microscopy combined with EDX microchemical analysis [113]. Recent studies have shown that image processing enables identification of subpopulations of components based on chemical composition [114]. Complementary information, such as a particle size distribution or averaged reactive surface area, can be measured and attributed to these subpopulations. This method was recently applied to explain the reaction rates of chemically distinctive fly ash components in both model systems [115] and cement pastes [109]. Moreover, the proportions of different compositional groups in a range of fly ashes have been shown to correlate to compressive strength development in mortar bars [116]. Blast furnace slags [117] and calcined dredging sediments [38] have also been studied by this method. The application of the technique may very well find its way to other systems as well. Drawbacks are that the technique is inherently limited by the spatial resolution of the EDX interaction volume (1-2 µm) and that the optimization of the image processing routines can be time-consuming if done manually. Further progress on the latter may be made by adopting approaches rooted in artificial intelligence such as supervised machine learning for object recognition [118].

Advances in sub-micrometer scale imaging may well deliver more insight into SCM reaction mechanisms and features such as lattice defects that control reactivity. Detailed characterization of SCMs and their reaction products down to the nanoscale has been pursued, taking advantage of the continuous development of advanced characterization techniques accessible in specialized research facilities. Combined with focused ion beam (FIB) milling to prepare sample foils, scanning transmission electron microscopy has enabled observation of hydration product morphologies and unambiguous determination of their composition in blended cements that contain sub-micrometer SCMs such as silica fume or metakaolin [119]. FIB was also used to prepare thin slits in a blast furnace slag surface. These were used as so-called microreactors to observe the early hydration of the slag in alkaline solutions by SEM [112]. More quantitatively, 3D images of dissolving SCM surfaces have been acquired to calculate dissolution rates using nanoscale surface topography measurement techniques such as atomic force microscopy (AFM) or vertical scanning interferometry (VSI) [60,120]. These techniques not only measure bulk dissolution rates, but, by visualizing the retreating surface, can also track the effect of lattice defects, inclusions and other nanoscale features in crystalline materials. 3D images of entire hydrating C_3S and C_3A particles at nanoscale resolution has been made possible by recent developments in synchrotron imaging techniques. Nanoscale X-ray tomography, ptychographic imaging and X-ray fluorescence microscopy were recently used to study the early hydration of C_3S [121] and C_3A [122] in 3D at unprecedented resolution, as shown in Figure 4. These techniques may also be applied to observe how individual SCM particles react.

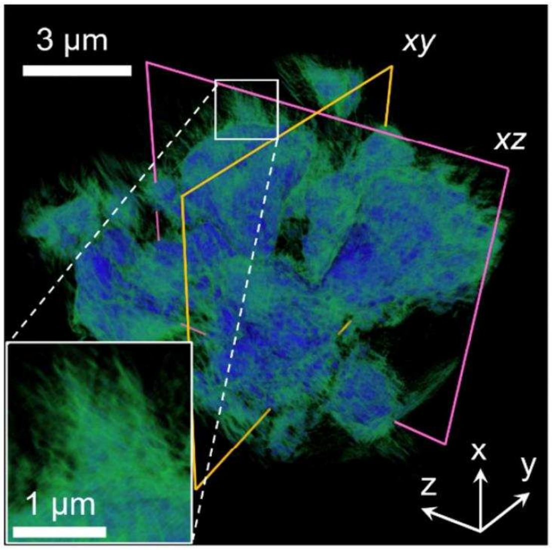

Figure 4. 3D X-ray nanotomography reconstruction of C_3A particles hydrated in the presence of gypsum for 143 min. C_3A is shown in blue, hydration products in green. Reprinted from [122] with permission from Elsevier.

3.2 Advances in SCM Reactivity Testing

In the long run, advances in in-depth characterization techniques are key to fundamentally understand, and eventually predict, the behavior and performance of blended cements based on fundamental structure-property relationships [123]. However, in the short term, more practical tests are needed to expedite the development of the next generation of high performance, durable and sustainable cements. In this respect, a SCM screening reactivity test should be practical, reproducible, applicable to a wide range of SCMs and deliver a relevant result to evaluate the performance of the SCM in cement. Unfortunately, most of the existing test methods are found to fall short on one or more of the test method requirements, in particular regarding the range of SCMs covered and correlation to performance. In case of methods that measure “reactive silica” or consumption of $Ca(OH)_2$ as a proxy for SCM reactivity, such as the Chapelle or the Frattini tests, correlation to the compressive strength development of benchmark mortar bars is not clearly apparent and cannot be extended to cover both pozzolanic and latent hydraulic materials [11,124,125]. In addition, a common weakness is the robustness of test methods due to deficiencies in protocol descriptions or reagent specifications [126]. On the other hand, test methods based on strength development, such as the ASTM C 311 strength activity index, often require 28 to 90 days before the contribution of the SCM becomes evident and cannot distinguish between physical packing or filling, and chemical reactivity effects, which can eventually lead to ambiguity as regards to material classification [12,127].

In a concerted effort to make progress on improving SCM reactivity test methods, both RILEM and ASTM initiatives were set up to evaluate standardized and newly-proposed SCM reactivity tests against criteria such as correlation to strength development or interlaboratory reproducibility. In the work of the RILEM TC 267-TRM, a wide range of SCMs was considered, including both pozzolanic and latent hydraulic materials. The results indicated that measurements of heat release or bound water in so-called R^3 model pastes performed best to quantify both the pozzolanic and latent hydraulic reactivity simultaneously [124]. The R^3 model paste supplies an excess of $Ca(OH)_2$ and water to measure the unconstrained reaction of the SCM. Additional alkali, sulfate and calcite are added to simulate a typical portland cement reaction environment. The pastes are cured at 40°C to accelerate the SCM reaction. Elimination of portland cement enables measurement of the reaction of the SCM directly by robust, accessible properties such as heat release or bound water. Moreover, mutual interference between clinker and SCM reactions can be avoided. The R^3 test method was first applied to calcined kaolinitic clays by Avet et al. [128], showing good correlation to compressive strength for cumulative heat, bound water and also chemical shrinkage results. This is illustrated for the R^3 model paste cumulative heat at 1 day and compressive strength at various ages of standard EN 197-1 mortar bars in which portland cement was replaced by 35% of calcined clay and 15% of limestone in Figure 5.

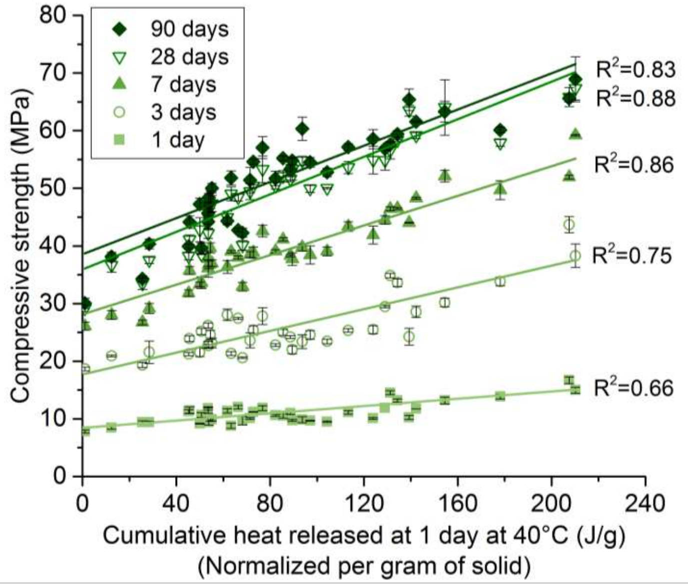

Figure 5. Correlation between mortar strength (20°C) and cumulative heat released at 1 day of hydration for isothermal calorimetry run at 40 °C for calcined clay-portlandite-limestone R^3 model systems.

Reprinted with permission from [129].

Applied to a broader range of conventional SCMs of comparable particle size distribution as portland cement, the correlation of the test results to the mortar compressive strength at 30 wt% cement replacement was shown to hold, first by Snellings and Scrivener [11] and subsequently by the more extensive work of the RILEM TC 267-TRM [124]. To distinguish between pozzolanic and latent hydraulic materials, Suraneni and Weiss [130] suggested to complement the results with $Ca(OH)_2$ consumption as measured by thermogravimetry. The phenomenological explanation of the strong correlations between the measured heat release, chemical shrinkage and bound water in the R^3 test is that these are all direct manifestations of the formation of hydration products. The solidification of water by formation of common cement hydrates is accompanied by a remarkably constant reaction enthalpy [131], which is proposed to be behind the convergence of trends for bound water and isothermal calorimetry.

4. Understanding the Impact of SCMs on Concrete Durability

As discussed in previous sections, SCMs modify the type of hydration products forming in portland blended cements and can also improve particle packing, pore refinement and reduce connectivity of pores in concrete produced with them [132]. It is well known that the combined response to aggressive agents of hydration products present in blended cements, for example their chloride binding capacity [133–135], along with improved transport properties, enhances the long term performance and durability of SCM-containing concrete [136]. Detailed information about the characteristics, including permeability and chemical durability, of concrete with conventional SCMs such as blast furnace slag, fly ash, natural SCMs and alternative SCMs, has been recently published in the state-of-the-art report of the RILEM Technical Committee (TC) 238-SCM [137]. Here, a summary of the recent advances on durability of concrete containing natural or new sources of SCMs is presented.

4.1 Durability of Concrete Containing Natural SCMs

The durability of concrete with natural SCMs, such as calcined clays [138] and volcanic ashes and tuffs [139], has been extensively assessed, as outlined in the RILEM TC 238-SCM state-of-the-art report [137]. It is well-established that natural SCMs contribute to the long-term compressive strength development of concrete and overall can significantly improve durability, which is one of the main incentives for their use in concrete production [140]. There is a good consensus that concrete containing natural SCMs can present low chloride permeability [141,142], high sulfate resistance [143], and in most cases reduction of alkali-silica reaction [144]. However, due to the variability in chemical composition and reactivity of natural SCMs, their effects on the properties of cement and concrete can vary significantly depending on the source and amount of the natural SCMs used.

There are a limited number of reports on durability of concrete containing new sources of natural SCMs [63], as most of these materials have previously been used for other purposes (pumice [145] and several agricultural wastes [146] have been used as aggregates, for example), or their applicability as SCMs was not identified until recent years (e.g. dredged sediments [38]). In spite of this, the existing knowledge about the correlations between the type of hydration products forming in cements blended with conventional SCMs and their response to different aggressive agents may be transferred to concrete containing new sources of SCMs. Hence, more studies focusing on detailed evaluation of the microstructural features, including phase assemblage evolution, pore structure, and chemical resistance of cement containing natural or new sources of SCMs are urgently needed, to elucidate how concrete containing these materials might perform in service. In addition, more studies determining the corrosion mechanism of steel reinforcing bars embedded in concrete with natural SCMs are urgently needed, particularly evaluating the effect of carbonation and/or chlorides on the service life of reinforced concrete. A recent study by De Weerdt et al. [147] demonstrated that carbonation reduces the alkali metal concentration in the pore solution of concrete, coupled with an increase in chlorine and sulfur concentrations, which can further accelerate corrosion in carbonated concrete.

4.1.1 Natural Zeolites and Pumice

Clinoptilolite is one of the most common zeolite minerals and, as such, also one of the most widely used zeolites in production of concrete. Addition of 10 -20% improves chloride chemical binding in concrete via formation of Friedel's salt [148], which explains the reduced chloride penetration reported in concrete containing this natural SCM [149]. In combination with chemical admixtures (e.g. superplasticizers and/or air entraining agents), clinoptilolite-type zeolites decrease the water penetration, while increasing freeze-thaw resistance of concrete [150,151]. Good chemical resistance has also been reported [152] for clinoptilolite-containing concrete when exposed to $MgCl_2$, NH_4Cl, Na_2SO_4, and HCl, when compared with plain portland cement systems. Their effect when concrete is exposed to H_2SO_4 is strongly dependent on the amount of zeolite added [153]. Concrete containing this SCM also exhibits high susceptibility to carbonation when tested under accelerated (5% CO_2) conditions. However, under natural carbonation conditions, carbonation resistance was much better, and a carbonation front was solely identified at high zeolite contents (25 wt.% replacement) after 15 months of exposure [153].

The addition of ground pumice as an SCM in concrete reduces early age compressive strength, along with a decrease of water absorption, sorptivity, and volume of permeable voids at extended curing times [154]. Madani et al. [155] identified in blended concrete with high volumes of pumice (up to 60 wt.%) negligible differences in chloride diffusivity, water absorption and volume of permeable voids, compared with plain portland cement concrete, after 28 days of curing; however, improvements in all these properties were observed after one year of curing. The addition of low contents of silica fume (e.g. 3 wt.%) significantly improves the chloride resistance of ternary mixtures of portland cement-pumice-silica fume at early ages. This is associated with a reduced water absorption and refined microstructure development [155].

An increase in the durability against magnesium sulfate attack has been observed in pumice-containing systems [153,154,156], as well as a reduction in shrinkage strain at longer drying durations. Good resistance to sulfuric acid attack has also been reported for pumice-containing concrete [153]. Concrete with less than 10% addition of pumice also presents a carbonation resistance comparable to that of concrete without SCMs, when tested under accelerated (5% CO_2) and natural testing conditions [153]. Increasing the pumice content significantly reduced the carbonation resistance of these materials.

4.1.2 Non-Kaolinitic Clays and Sediments

The majority of studies on non-kaolinitic clays have centered on determining the best pre-processing treatments to improve their reactivity and the phase assemblages forming upon blending with portland cement, as was discussed in previous sections. Studies of durability of concrete containing uncalcined, non-kaolinitic clays are mainly centered on determining their effects when present as a contaminant in aggregates [157,158], although in recent years, these materials have also attracted interest as nanomaterials with the potential to enhance strength and durability of concrete [159]. For example, Langaroud et al. [160] identified that small additions of a montmorillonite-based nano-clay (i.e. 95% purity and maximum size of 1-2 nm) (< 3%) in self-consolidating concrete, with and without inclusion of other SCMs (e.g. rice husk ash, silicate fume, blast furnace slag or fly ash), promotes significant reductions of the water and chloride permeability, particularly at 3% addition.

There are a limited number of durability studies of concrete containing calcined sediments. Amar et al. [161] identified that mortars with 10% portland cement substitution by calcined dredged sediments present a similar freeze-thawing, chloride permeability and sulfate attack performance compared with materials without SCMs. Higher contents of this SCM led to a significant reduction in durability performance of these materials. This was associated with increased porosity and water permeability at high replacement levels (Figure 6). Safer et al. [162] observed in concrete with up to 20% calcined dredged sediment a comparable resistance to H_2SO_4 attack to that of concrete without SCMs. Snellings et al. [39] reported a comparable hydration products phase assemblage in plain cement systems and those with up to 30% of a flash calcined dredged sediment. Van Bunderen et al. [163] also identified for concrete with 30% calcined sediment an increased resistance to chloride ingress compared to portland cement without SCMs, consistent with a refined pore structure as a result of the pozzolanic reactions; however, the scaling resistance was reduced when evaluated in presence of de-icing salts.

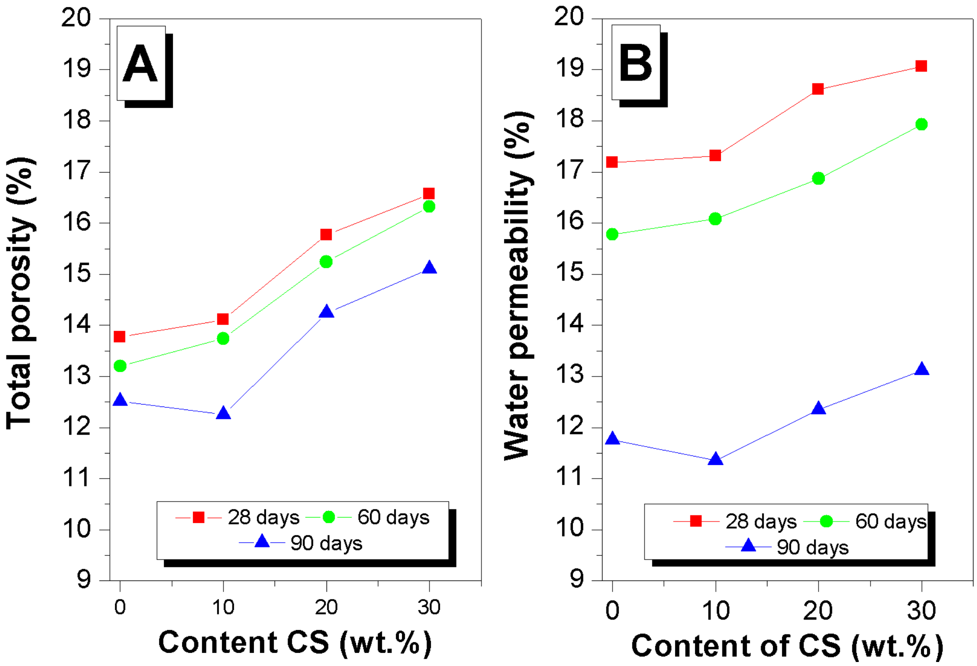

Figure 6. Total porosity determined by mercury intrusion porosimetry, and water permeability of mortars containing calcined dredged (CS) sediment, as a function of the time of curing. Data from [161].

The differences in performance reported among the few durability studies of calcined sediment SCMs when testing concrete with different amounts of this SCM are likely a consequence of combined variations in the chemical composition of sediments from different sources and the calcination processes used, which modifies their physical properties and their reactivity. Further studies about the factors governing the durability of these systems are required to identify strategies to mitigate their potential damage, particularly when exposed to freeze-thaw conditions.

4.1.3 Portland Cement-Limestone-SCMs

For decades, portland limestone cements have been widely used globally. Limestone powder has a relative low cost, low energy consumption and reduced global warming potential. The filler, dissolution, and chemical effects of limestone powder in concrete are dependent on the particle size, dosage, dissolution, and mineral composition of the cement, among other factors that have been extensively documented, as outlined in a recent review by Wang et al. [164]. The mechanical and durability properties of portland limestone cements are also discussed in that review, where it is highlighted that a high content of limestone in the concrete increases susceptibility to sulfate attack, particularly thaumasite formation [165]. For this reason, the amount of limestone addition in Europe is limited up to 20% limestone for CEM II/A-L and up to 35% for CEM II/B-L, and blended portland cements containing up to 15% limestone have recently been introduced into Canada and the US [166] .

Palm et al. [167] identified that low-water concrete (e.g. water/cement ratio of 0.35) with higher contents of limestone than those allowed in European and American standards (between 35 wt.% - 65 wt.% of CEM I replacement) is comparable to concrete designed according to EN 206 [4]. A lower chloride permeability was obtained in concrete with the highest compressive strength, consistent with a reduced content of air in the mixes. However, freeze-thaw resistance was reduced at low air contents. Concrete with up to 50 wt.% limestone presents good sulfate resistance (Figure 7), if designed with low water contents, and optimized packing density [168]. This is true even in samples tested at 8°C (Figure 7b), where thaumasite precipitation could be expected in the presence of high concentrations of SO_4^{2-} (up to $30\,g{\cdot}L^{-1}$), Ca^{2+}, CO_3^{2-}, and silicic acid, which are the conditions prevailing in the tested systems. Sulfate resistance can also be improved by addition of other SCMs. It has also been reported that the use of limestone with high $CaCO_3$ content particularly facilitated thaumasite formation. Rezvani et al. [169] demonstrated that the content, chemistry (e.g. varying content of CaO, SiO_2, Al_2O_3, Na_2O, among others), and mineralogy (e.g. 97.8 – 66.9 wt.% $CaCO_3$) of the limestone influences the drying shrinkage-related microcracking of concrete with up to 70 wt.% limestone. Rezvani et al. [169] developed an analytical model, integrating mechanics of porous materials and thermodynamics, to predict drying shrinkage of these materials.

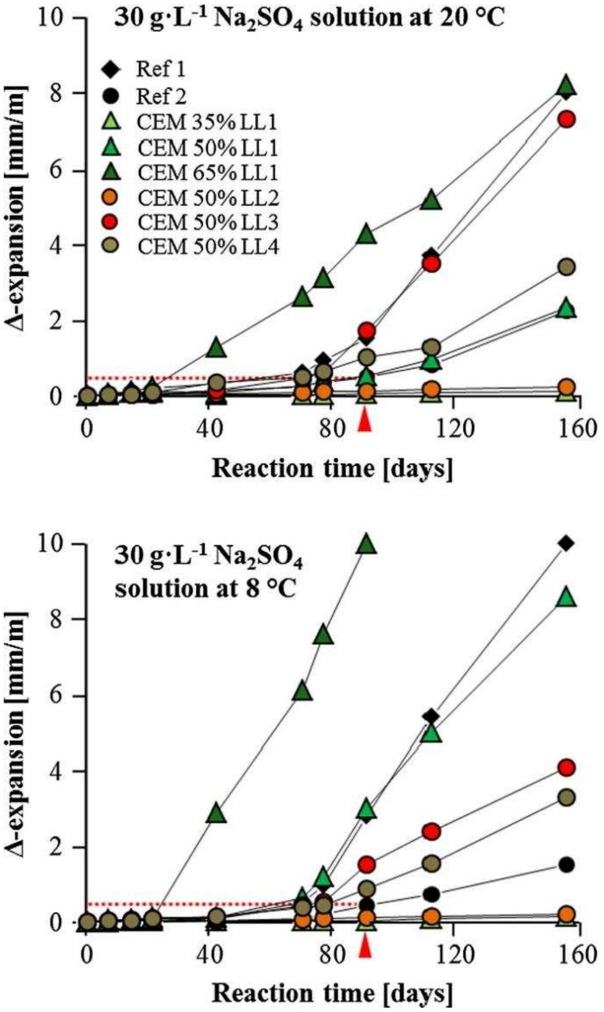

Figure 7. Strain development of mortars after 158 days of storage in a Na_2SO_4 solution. Expansion is reported as Δ-expansion, relative to the mortars immersed in a $Ca(OH)_2$ reference solution at 20 °C. The SVA[1]-guideline limit for a high sulfate resistance of the test specimens is ≤0.5 mm/m after 91 days

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[1] SVA is the sulfate resistance testing method of the committee of experts of the German Institute for Civil Engineering described in [170].

(marked with the dotted red line and the red triangle) [170]. LL corresponds to limestone with $CaCO_3$ of 97.5% (LL1), 79.7% (LL2), 77.5% (LL3), and 77.4% (LL4), respectively. Reprinted from [168] with permission from Elsevier.

As mentioned earlier, the LC^3 system is attracting particular attention from academia and industry. Scrivener et al. [43] reported that limestone calcined clay cement (LC^3)-based concrete presents excellent resistance to chloride penetration, mitigation of alkali-silica reaction, and durability in the presence of sulfates. This is associated with a high degree of pore refinement, which is dependent on the calcined kaolinite content [45]. More pore refinement is observed in systems produced with clays with up to 50 wt.% kaolinite. This pore refinement particularly enhances the chloride resistance, as it has been observed that for some LC^3 formulations, their total binding capacity is comparable to that of portland cement systems in spite of some Friedel's salt formation [171]. Shi et al. [172,173] identified that in LC^3 systems the chloride binding capacity is actually improved with the addition of metakaolin due to an increased formation of Friedel's salts, compared with plain portland cement systems. This is a consequence of metakaolin acting as an additional source of aluminum. The differences in results between these studies are most likely due to the differences in purity of the clays or calcination process used to produce the metakaolin. The content of soluble calcium in these systems also seems to be a determining factor in the chloride binding capacity of materials with limestone, independently of inclusion of metakaolin [173]. It is interesting that studies reveal that the use of high-grade clays is not necessary to obtain significant improvement in chloride penetration resistance in LC^3 systems [174], due to the higher resistivity [44,174] and refined pore structure.

A high resistance to sodium sulfate attack has also been identified for these materials [175], produced with either calcined kaolinite or calcined mortmorillonite. This was attributed to the consumption of portlandite by the pozzolanic reactions of the calcined clays and the dilution of the portland cement clinker, leading to a lower amount of calcium available for the secondary formation of gypsum and ettringite. Formation of thaumasite was not observed in limestone-metakaolin-portland cement systems tested at 5°C, consistent with the observations reported by Mirvalad et al. [176].

Shi et al. [177] observed higher carbonation resistance of LC^3 materials, comparable with those solely blended with limestone, consistent with the refined pore structure reported for LC^3 systems [45]. In these materials, the changes in pH detected by phenolphthalein indicator are associated with a two-step carbonation of the C-S-H phase. Upon carbonation of high-Ca C-S-H, an initial depletion of Ca^{2+} ions in the interlayer space occurs. As carbonation progresses, the resultant C-S-H with a lower calcium content than the original C-S-H degrades to form a silica gel and calcium carbonate (Figure 8) [177]. LC^3-based concrete showed a comparable performance to that observed for concrete containing fly ash, but presented higher carbonation rates than concrete blended with blast furnace slag [178].

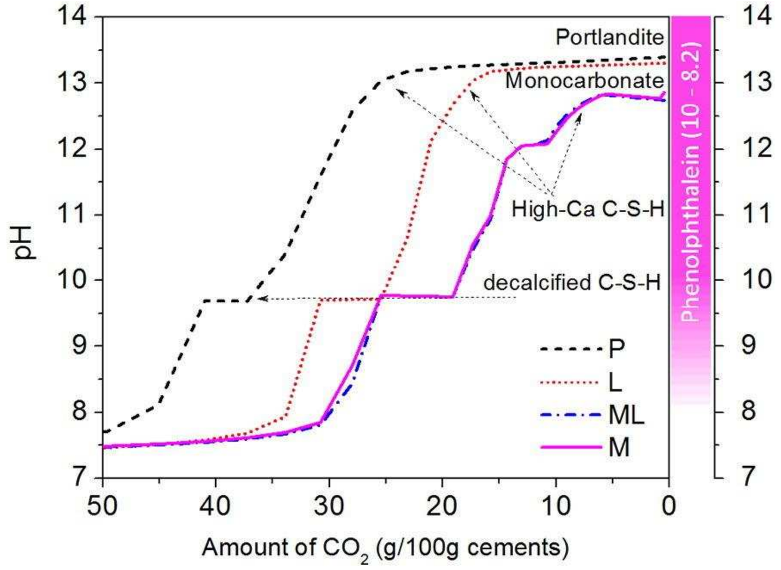

Figure 8. pH profiles related to the changes in phase assemblages predicted by thermodynamic modeling. The right bar indicates the gradual color change of phenolphthalein from fuchsia to colorless

upon pH changes from 10 to 8.2. *P* corresponds to 100 wt.% white portland cement; L – 68.1 wt.% white portland cement + 31.9 wt.% limestone; *ML* to 68.1 wt.% white portland cement + 25.5 wt.% metakaolin + 6.4 wt.% limestone; and *M* – 68.1 wt.% white portland cement + 31.9 wt.% metakaolin. Reprinted from [177] with permission from Elsevier.

Global scarcity of high-grade limestone has motivated investigation on other carbonate sources for production of concrete. Dolomite ($CaMg(CO_3)_2$) in particular has been identified as a potential substitute of limestone. Zajac et al. [178] demonstrated that the reaction of dolomite in portland cement pastes leads to formation of comparable phase assemblages to those of limestone added cements. Dolomite acts as a magnesium source aiding formation of hydrotalcite, which contributes to the compressive strength development of these systems. Hydrotalcites can also play an important role in improving durability performance of concrete. Ke et al. [179] showed that hydrotalcites can take up chloride from highly alkaline solutions with different initial $[Cl^-]/[OH^-]$ ratios, via a combined surface adsorption and ion exchange mechanism. Machner et al. [135] assessed the chloride binding capacity of materials with 40 wt.% portland cement replacement by either limestone or dolomite, in combination with metakaolin (5 wt.%), and identified that formation of hydrotalcite in dolomite-containing systems has a positive effect on the chloride binding capacity, to a similar extent as the Friedel's salt formed in systems containing limestone. It has also been observed [180] that hydrotalcite forming in dolomite-metakaolin-portland cement systems, withstands leaching and carbonation, which can potentially be beneficial for the durability of the resulting concrete.

In a recent study [47] evaluating the phase assemblage evolution of calcium and magnesium carbonate-metakaolin-portland cements, it was identified that these carbonates have a comparable effect on hydration, as both minerals used in that study contained calcite. The amount of calcite present was sufficient to promote hemicarbonate formation, and significant differences in pore refinement and distribution of portlandite and silicates were observed in the carbonate-containing specimens, compared with reference samples containing quartz. This indicates changes in the pozzolanic reaction of metakaolin in presence of carbonates, which might impact performance evolution of these composite cements.

Other ternary systems that have attracted significant interest are blends of portland cement containing blast furnace slag and limestone, and recent studies have been focused on determining factors influencing their phase assemblage evolution [181] and their impact in performance of these materials [182]. Proske et al. [183] identified for these systems comparable carbonation rates to those reported for CEM III/A, a good resistance against chloride migration, and a significant decrease in drying shrinkage and creep deformation compared with concrete without SCMs. However, a higher susceptibility to damage due to freeze-thaw was observed. The freeze-thaw performance significantly improved when the water content of these composite concrete was reduced. Similar results were observed by Zhang et al. [184], who identified a reduction in the carbonation and freeze-thaw resistance of blends with higher volumes of slag replacement, although addition of limestone slightly enhanced the performance of these materials. In pre-carbonated specimens exposed to freeze-thaw cycles, a reduced scaling resistance and higher internal damage was identified compared with non-carbonated specimens [184,185].

Durability of portland cement-SCM-limestone based concrete requires further investigation, so that mitigation strategies can be adopted to enhance their performance particularly against carbonation and freeze-thaw.

4.2 Durability of Concrete Containing By-Product SCMs

The recent reviews by Mo et al. [186] and Martirena et al. [187] provide a state-of- the-art overview about concrete produced with SCMs derived from farming waste residues, including ashes from bamboo, wheat, banana leaf, and elephant grass, among others. It is evident from these reviews that there is little or no systematic understanding about the effects of these potential SCMs on the durability of concrete containing them. This is consistent with their few practical applications as SCMs.

However, some promising results have been published. For example, Bahurudeen et al. [188] identified that the addition of sugar cane bagasse ash in concrete increased the resistance to chloride ingress and gas penetration in concrete. This positive effect has also been observed in ultra-high strength concrete (160 MPa) with up to 15 wt.% replacement of cement by sugar cane bagasse ash, consistent with significant reduction of permeability, particularly when high temperature (90°C) steam curing is applied during the first 24 h after mixing, although steam curing would usually lead to a more porous structure [189]. An improved resistance to alkali-silica reaction in materials containing sugar cane bagasse ash has also been identified [190].

Czarnecki et al. [191] evaluated the carbonation resistance of concrete produced with different contents of a calcareous fly ash from non-standard circulating fluidized-bed combustion (FFACa) from coal combustion in a circulating fluidized bed boiler. Using a lower water/binder ratio reduced the carbonation susceptibility of the concrete, so that concrete designed with a water/binder of 0.45 and 15% of FFACa presented comparable carbonation depth to concrete without SCMs.

Paul et al. [192] published a recent review on materials containing waste recycled glass and showed that most durability studies of concrete containing this SCM have been centered on alkali-silica reaction (ASR), which is strongly dependent on the particle size of the waste glass used, so that the pozzolanic reaction can prevail over ASR for finely ground glass cullet (Figure 9). In most studies, a reduced expansion has been reported in materials blended with powdered waste glass. A low water absorption, along with a high resistance to freeze-thaw and low chloride ingress, have also been reported for concrete with both powdered and sludge waste glass.

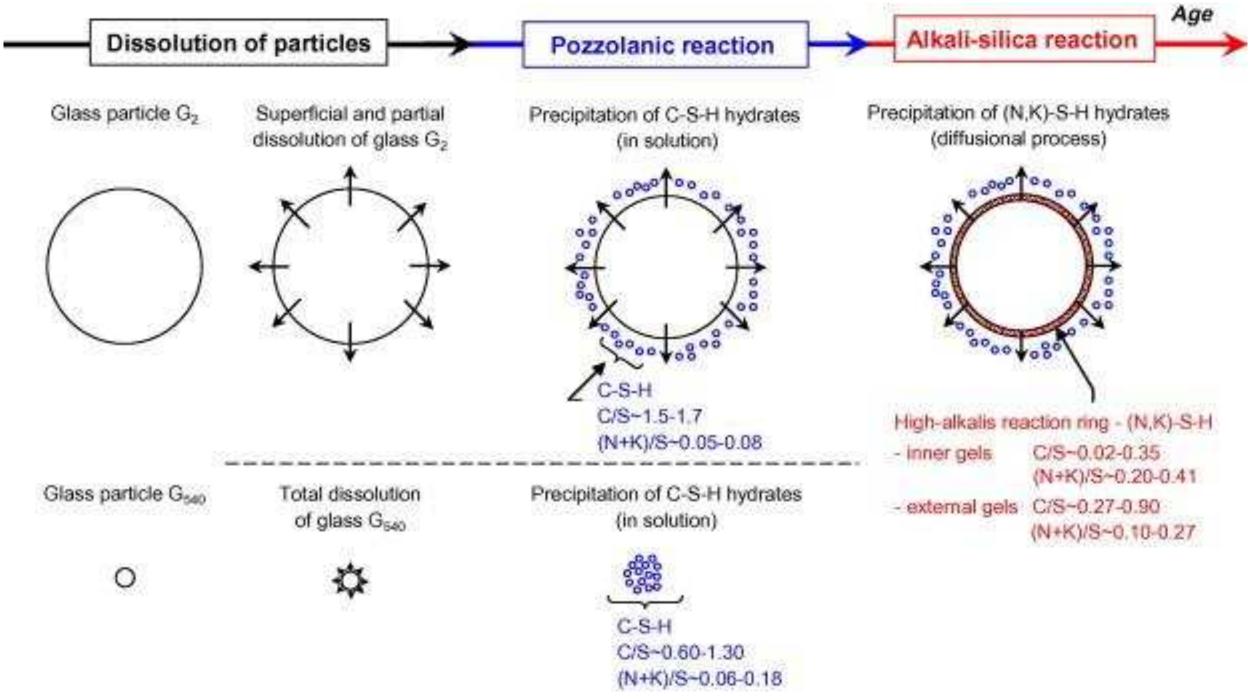

Figure 9. Successive reactions of coarse and fine glass particles. Reprinted from [193] with permission from Elsevier.

4.3 General remarks about Durability Testing of Concrete with New SCMs

Although new sources of SCMs have been identified, and, in some cases, excellent durability performance has been reported, there are some barriers limiting their immediate uptake, including the question of whether standardized testing methodologies are applicable to evaluate durability performance under accelerated conditions. For instance, Auroy et al. [194] in a recent study concluded that, considering the changes in phase assemblage induced when cements blended with slag or fly ash are exposed to 3% CO_2 or 0.04 % CO_2, accelerated carbonation testing at 3% CO_2 is sufficiently representative of long-term carbonation when adding these SCMs. However, Leemann et al. [195] identified significant differences in carbonation coefficients determined under different exposure conditions for mortars and concrete containing slag and silica fume, which underperform when tested under accelerated carbonation conditions (1% and 4% CO_2) compared with field observations (Figure 10). This is mainly a consequence of the level of saturation of the concrete, so that at a moderate relative humidity (RH) (57% RH) no significant influence of CO_2 concentration has been identified regarding the carbonation ranking of concrete produced with nine different portland blended cement types [196]. This is not the case when accelerated carbonation of concrete is induced at 80% RH due to an increased volume of pores filled with water. Consequently, an increase of RH in accelerated testing does not improve the transferability of the results to natural carbonation. Such observations are of particular importance as concrete with SCMs might perform significantly better in conditions inducing rebar corrosion, than indicated by accelerated carbonation tests. These discrepancies highlight the fact that phase assemblage, pore solution chemistry, and transport properties play a significant role in how degradation mechanisms proceed. Hence, to determine durability of concrete, such factors need to be coupled with reactive transport models so meaningful results from accelerated tests can be obtained. There have been significant advancements in the application of thermodynamic modeling of phase assemblages to the understanding of durability in SCM-blended materials when exposed to sulfates [197], carbonation [147], and chlorides [198], and in linking these models to reactive transport simulations [199–201], However, this remains an area in need of further development and insight for concrete produced with conventional SCMs and more so for those with new SCMs.

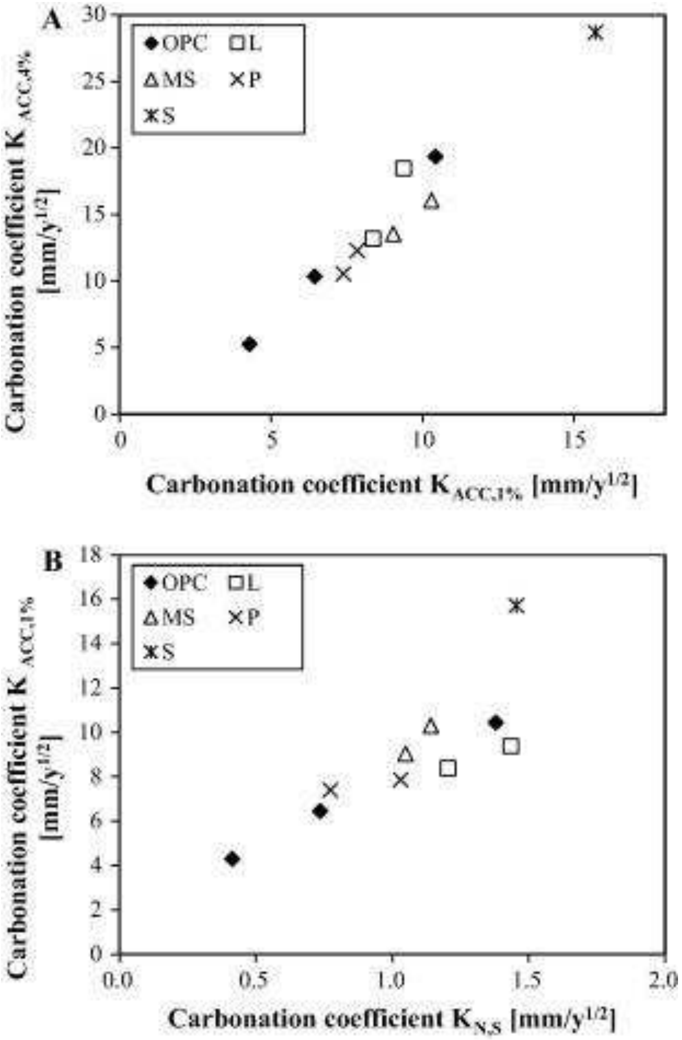

Figure 10. (A) Carbonation coefficient K_{ACC} of mortars at 4% CO_2 versus carbonation coefficient K_{ACC} at 1% CO_2 ($R^2 = 0.96$). (B) Carbonation coefficient K_{ACC} at 1% CO_2 versus carbonation coefficient $K_{N,S}$ in sheltered, outdoor exposure ($R^2 = 0.69$). *OPC* correspond to mortars based on CEM-I, *L* mortars with

added limestone, *MS with* added microsilicate, *P* with added portlandite, and *S* mortars based on CEM III/B. Reprinted from [195] with permission from Elsevier.

The approach for assessing durability of concrete with new sources of SCMs has mainly centered on developing parametric studies for given formulations at specific exposure conditions, without much insight explaining the mechanisms governing the performance of those materials considering their chemistry and/or transport properties. Hence, it is difficult to transfer the decades of knowledge gained on durability performance of concrete with conventional SCMs. In order to elucidate the mechanisms leading to different types of degradation in concrete with SCMs of any nature, a deeper understanding of the chemical and transport phenomena taking place at different scales needs to be developed. This will enable the creation and adoption of the suitable testing methodologies for the reliable assessment of durability performance of concrete with alternative SCMs, which will underpin the development of more accurate models for their long-term performance prediction.

Considering the diversity of new sources of SCMs, the most tractable approach is probably to develop and validate the core models for materials containing conventional SCMs, with a focus on relating performance to hydrate assemblage and pore structure. The application of such models to concrete with new sources of SCMs will then be much more straightforward on the basis of readily-determined material parameters, e.g. the nature and fractions of the hydrate phases formed and the pore geometry and pore fluid chemistry, rather than fully re-building a model specific to each different SCM.

The lack of in-service history to validate the observations made from accelerated durability tests is another challenge for the uptake of new SCMs. The prediction of the long-term performance and durability of modern and future concrete containing new or alternative SCMs, within time-scales relevant to their immediate application, is one of the main scientific challenges that needs to be resolved to bring the necessary confidence for their use in practice. Hence, for blended cements containing new or alternative SCMs, whose phase assemblage evolution and pore structure fall within well-established trends for the known historical record of conventional SCMs, it is sensible to think that they will perform at least equally to those materials that have been used for several decades.

5. Insights, Recommendations, and Conclusions

SCMs have been used in concrete mixtures for decades to improve performance such as increased long-term compressive strength, enhanced long-term durability, reduced cost, and reduced environmental impact. The cement and concrete industries have become reliant on these materials, particularly on those with low cost and high availability from industrial waste streams. However, as demand for conventional SCMs increases and supply decreases, there is a great need to find new sources of materials that provide comparable or superior properties to the highly utilized fly ash and slag sources. At the same time, it is important to consider maximizing resource efficiency and sustainability, making use of wastes from different industries that currently have little or no commercial value.

It is clear that research into new sources of SCMs, their reactivity, and their impact on concrete properties has been increasing in recent years and has great likelihood to further increase as the demand for these materials grows. Ideally, we could directly translate the extensive body of knowledge on commonly-used SCMs to new material sources, but it is becoming apparent that new research is necessary, especially in some areas. Despite the great technical potential of some of the new SCMs, there are some barriers limiting their uptake such as reduced reactivity, low production speed, scarcity of resources, and more quality control needs, compared to conventional SCMs. More studies are required to identify potential solutions to these barriers, as well as to quantify the environmental and economic savings that utilization of new SCMs can offer. This will underpin changes in policy so that incentives for their use can be implemented in future infrastructure projects. The inclusion of new SCMs in existing or new standards is imperative to enable their widespread use in the years to come. This might be achieved more promptly for natural SCMs such as pumices and calcined clays, due to their homogeneity and known chemistry.

The implementation of some SCMs is contingent on a better understanding of their reactivity, particularly in the case of impure calcined clays. An improved understanding of the reactivity of the minerals in these complex, heterogeneous materials is needed. Likewise, when calcined clays and other SCMs are combined with limestone and cement, the ensuing reactions, microstructural development, and their impacts on durability need further investigation. These so-called LC^3 and similar systems hold great promise as low-cost, high-availability SCMs, and further research will facilitate their implementation. Some new SCMs derived from wastes may potentially contain heavy metals (e.g. municipal solid waste bottom ashes or some non-ferrous slags) that might limit their applicability as infrastructure materials. It is then important that more studies are focused on understanding the potential mobility of those species within concrete to ensure the safe use of new SCMs.

Alongside the exploration of new materials is the need for new standardized tests and standards governing their use. Existing test methods for pozzolanic reactivity have repeatedly been found to be either ineffective at predicting performance or lack robustness. New test methods are being developed, and we expect to see these find their way into practice in the coming years. Likewise, methods to characterize the impact of SCMs on durability, such as resistance to carbonation, need to be revisited and revised in the context of new materials and systems. Further research on test methods, for SCM characterization and for concrete durability, will facilitate the development of new standards allowing for a greater diversity of allowed SCMs in our evolving concrete mixtures.

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